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(54) Title: A PROCESS FOR BLEACHING PULP WITHOUT USING CHLORINE-CONTAINING CHEMICALS (57) Abstract The present invention relates to a process for bleaching pulp which has been digested and oxygen-delignified, using methods which preserve viscosity and strength, to kappa numbers lower than 12, preferably lower than 10, without using chlorine-containing chemicals and employing a bleaching sequence containing at least 3 bleaching stages, whose first three stages are QPZ, preferably containing an additional bleaching stage, appropriately in the form of a P-stage, this chlorine-free process being environmentally optimised, inter alia by keeping the total quantity of filtrate leaving the bleaching plant at a low level.		

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A process for bleaching pulp without using chlorine-containing chemicals

The environmental protection authorities are making ever more stringent demands on the pulp industry to decrease the use of chlorine gas in bleaching. Permitted discharges of organic chlorine compounds (AOX) in the waste water from bleaching plants have been gradually lowered and are now at such a low level that the pulp factories have in many cases stopped using chlorine gas. Instead, only chlorine dioxide is used as a bleaching agent. In achieving the same bleaching effect, chlorine dioxide forms smaller quantities of AOX than does chlorine gas. However, the use of chlorine dioxide has likewise been questioned. On the one hand the environmental protection authorities in certain countries require that the discharges of organic chlorine compounds be reduced to such a low level that the requirements can hardly be fulfilled even if only chlorine dioxide is used for bleaching. On the other hand, environmental movements in several countries, in particular in Germany, have persuaded consumers to demand paper products which have been bleached entirely without using either chlorine gas or chlorine dioxide.

The pulp industry is therefore searching for methods which permit pulp to be bleached without using these chemicals. One such method has been developed by the Swedish company Eka, which supplies bleaching chemicals to the pulp industry. The bleaching method, which is called LIGNOX (see SE-A-8902058), involves the unbleached pulp being first delignified with oxygen and then, after washing, being treated with EDTA, or other suitable chelating agent, in order to remove heavy metals bound within the pulp. The EDTA stage (Q) is followed by an intensive bleaching stage with peroxide (P), i.e. hydrogen peroxide. The charge of hydrogen

peroxide (H_2O_2) employed is relatively high, 15-35 kg per ton of pulp, depending on the brightness required and on the bleachability of the pulp. The time is quite long, 4 hours or longer, and the temperature high, 80-90°C.

However, the lignox method only provides a limited increase in brightness. Maximum brightness depends on the bleachability of the pulp and on the charge of peroxide. Brightnesses in the region of 80-82 ISO have been measured. To achieve higher levels of brightness, further bleaching stages are required over and above the peroxide stage.

In this connection, ozone is an interesting bleaching chemical. Several experiments have shown that if an ozone bleaching stage (Z) is introduced after a peroxide stage, a significant increase in brightness is achieved while at the same time the lignin content of the pulp is decreased. The latter point is important, since a pulp bleached with only peroxide or oxygen/peroxide still contains a relatively high content of lignin, which affects the brightness reversion tendency of the pulp. When warmed or irradiated with sunlight, the pulp yellows. If ozone is used, further lignin is removed, resulting in the brightness of the pulp becoming more stable.

Lenzing AG in Austria (see EP-A-441 113) has demonstrated how an ozone stage after a peroxide stage increases the brightness of sulphite pulp. If a peroxide stage is allowed to follow the ozone stage, a further increase in brightness is obtained (3).

Eka has shown that this is also the case for sulphate pulp (4). Oxygen-bleached sulphate pulp was treated with EDTA to remove heavy metals and subsequently the pulp was bleached with peroxide and ozone according to the sequence QPZ. With this sequence, brightnesses in the region of 82-87 ISO were achieved, depending on the type of pulp. By extending

the bleaching sequence with a further peroxide stage and bleaching according to the sequence QPZP, brightnesses in the region of 87-89 ISO were obtained, depending on the type of pulp, see "Non Chlorine Bleaching"; J. Basta, L. Andersson, W. Hermansson; Proceedings March 2-5, 1992 - Westin Resort - Hilton Head - South Carolina; Copyright by Miller Freeman Inc.

Thus, it is possible, using the sequences QPZ and QPZP, to achieve the levels of brightness which are required for pulp by the market, i.e. 89 ISO and higher, without using chlorine-containing bleaching agents. This provides interesting perspectives regarding both the effect of cellulose factories on the environment and the possibility of satisfying the demands of consumers for access to chlorine-free bleached pulps.

A prerequisite for achieving high levels of brightness while using moderate quantities of bleaching agents is that, prior to bleaching, the pulp should have been delignified to low kappa numbers, at least lower than kappa number 16. Normally, a deterioration in quality, in particular loss of fibre strength, is obtained if the delignification in the digester house and oxygen delignification are taken too far. However, using the modified digestion methods which have been developed in recent years, it has been found possible to achieve very low kappa numbers without loss of strength. For example, it is possible, using a modification of Kamyr's continuous digestion process MCC (modified continuous cooking), combined with MC-oxygen delignification, to achieve and go below kappa number 10 with softwood and kappa number 8 with hardwood, while retaining their strength properties.

The modification of the MCC process involves the "Hi-heat" washing zone in the lower part of the continuous digester also being utilised for counter-current digestion (see EP-A-476230). This is achieved

by heating to the full digestion temperature in the Hi-heat circulation and adding alkaline digestion liquid to this circulation. The total digestion time in countercurrent is thereby extended to 3-4 hours as compared with about 1 hour in conventional MCC. In this way a very low concentration of lignin is achieved by the end of the digestion, which provides improved selectivity in the delignification, i.e. the lignin of the wood is efficiently eliminated without the cellulose being significantly affected. The digestion and oxygen delignification can thus be carried out to very low kappa numbers without impairing the properties of the pulp.

A pulp line with a continuous KAMYR® digester equipped for modified digestion according to the above-mentioned method, MC-oxygen delignification and a diffuser-bleaching plant constructed for the sequence QPZ(P) is a preferred overall configuration of a line comprising a preferred embodiment of the invention. This preferred embodiment of a bleaching plant is shown in Figure 1.

Accordingly, a diffuser-bleaching plant is shown, which is constructed for the sequence QPZ and optionally an additional P-stage. The said bleaching plant consists of a transport conduit 1 for pulp which is indicated throughout as a thicker conduit, and which at the beginning of the bleaching plant leads to a washing press 2. Subsequently there is a chute and an MC pump with inlet conduits 4, 5 for the incorporation of EDTA (Q) and sulphuric acid. Also included in this Q-stage are a storage tower 6 with agitator 6A and a chute with an MC pump 6B. Next there is a washing tower 7 comprising a double-diffuser, which is a known KAMYR® washing apparatus. From this washing tower 7 the filtrate being voided from the bleaching plant is drawn off via conduit 8. After the washing tower 7 there is a chute with an MC pump in which vigorous admixture of

peroxide (H_2O_2), for a P-stage, takes place via conduit 10. Usually NaOH is added here, as well, in order to adjust the pH to the desired level. Next comes the reaction vessel for the P-stage 11, which vessel is fitted at the top with a double-diffuser wash. After the P-stage there is a chute with an MC pump with a supply conduit 14 for vigorous admixture of sulphuric acid. Then there is a mixer unit 16 for incorporating ozone gas (O_3), for the Z-stage, via conduit 15. Next there is a reaction vessel 17 for the pulp with the ozone, which vessel is connected by its upper attachment to a chute with a cyclone arrangement 18 in the upper part of which the ozone is drawn off in order to be rendered harmless in an ozone destroyer. The pulp, on the other hand, continues downwards and is pumped onwards to a second washing tower 20 in which the pulp is given a last wash, whereby in the preferred case sufficient brightness has been achieved after only three bleaching stages, QPZ. Backwater, at a temperature of about 50°C , is appropriately employed as the washing liquid in the last washing tower 20.

Fresh water is taken into the system, for example at a temperature of about 45°C , via a conduit 19 which leads to the P-bleaching tower 11 and there feeds washing liquid to the double diffuser, preferably to its second stage. An additional contribution can, if necessary, also be obtained from the last washing tower 20 via conduit 21A. The filtrate from the second stage in the latter double diffuser is recirculated, as washing liquid, via conduit 13 to the first stage in the said double diffuser. The filtrate from this double diffuser, in the P-bleaching tower 11, is led away via a conduit 12 which is attached to a heat exchanger, which exchanger is fed with steam 12A so that the filtrate is pre-heated before it is conveyed to the double diffuser (preferably the second stage) in the first washing tower 7. Here too, recirculation occurs

from the second diffuser stage to the first via a conduit 9. For the purpose of pH adjustment, sulphuric acid can be added to the said recirculation conduit 9 via a separate conduit 9A.

The small amount of waste liquid which is drawn off from the bleaching plant is taken out from this double diffuser via a conduit 8 from the first stage of the diffuser. If required, a separate conduit 8A can be taken from this waste conduit 8 to the washing press 2 for diluting the pulp after the washing press 2. This dilution liquid can also be obtained from the last washing tower 20 via conduit 21 and 2B. The filtrate from the latter washing tower 20 is also employed as washing liquid in the washing press 2 and in this case is conducted onwards via a separate conduit 2A. The filtrate from the washing press 2 is taken out via conduit 3 in order to be used in the oxygen delignification stage.

An indication of how a supplementary bleaching stage can be coupled in, in the event of even greater brightness being required than that which can be achieved using 3 stages, is given in the Figure in the area bounded by a broken line from X to Y. In the preferred example shown here, the fourth stage comprises an additional P-stage, so that a QPZP bleaching sequence is obtained. Like the P-stage described previously, admixture of hydrogen peroxide (and optionally NaOH as well) occurs in a chute with attached MC pump via a conduit 22, after which the pulp is pumped to the bleaching tower 23, which consists at the bottom of a reaction vessel and is fitted at the top with a washing diffuser. The wash water for the said washing diffuser is appropriately, as in the above-described case, backwater at about 50°C, which is supplied via conduit 25. The filtrate from the wash is then led away via a heat exchanger, which is attached to the outlet conduit 24, and is led, at the

appropriate temperature, into the washing tower 20, where it is used as washing liquid.

In a fibre line with a bleaching plant as described above, fully bleached pulp with a brightness of 85-90 ISO can be produced without using chlorine-containing chemicals. The volume of waste water from the bleaching plant can be kept at a very low level, 5 to 10 tons per ton of pulp and possibly as low as about 3 tons of waste water per ton of pulp. Apart from foreign substances, such as metal ions, released in the Q-stage, the waste water only contains organic substances, released in the peroxide and ozone stages, and spent bleaching chemicals supplied to the bleaching plant, i.e. mainly sodium (Na) and sulphate ions (SO_4^{--}).

The composition of the dry substance of the bleaching plant filtrate is to a large extent the same as that of spent digestion liquid (black liquor) from the digester. It can therefore either be added to the black liquor or in some other way introduced into the chemical recovery system of the factory. For optimal heat economy, the bleaching-plant filtrate should be wholly or partially concentrated, for example by evaporation or freeze-crystallisation, before it is introduced into the recovery system. A part of the liquid can, if required, be employed, even without concentration, for dissolving the chemical smelt originating from the soda furnace. Heavy metals released in the bleaching stage are efficiently separated off by precipitation in the green liquor and are removed with the green liquor sludge during clarification or filtration. Any possible excess of sodium and/ or sulphur is removed in a known manner, for example by bleeding off from the chemical cycle, or is employed as alkali (NaOH) in the bleaching plant after complete oxidation of the sodium sulphide (Na_2S) present in the white liquor to sodium sulphate

(Na_2SO_4).

In order to achieve the lowest possible consumption of chemicals and heat energy and the best possible quality of pulp in association with the lowest possible quantity of waste discharge from the bleaching plant, it is important that the bleaching plant system is configured in the correct manner with regard to water management and washing efficiency after the individual bleaching stages.

This invention is a method for achieving the above object by a combination of a system for recirculating filtrate and supplying fresh water together with the use of washing devices of high washing efficiency after certain of the bleaching stages.

Laboratory experiments have shown that the washing efficiency¹⁾ after the Q-stage should be at least 85%, preferably 90-95%, in order to be able to achieve high brightness and the best possible pulp viscosity in subsequent peroxide stage(s). The reason for this is that even small quantities of metal ions in the peroxide stage cause decomposition of peroxide, which on the one hand increases consumption of peroxide and on the other lowers pulp viscosity.

A softwood sulphate pulp prepared in the factory using the modified MCC digestion technique and subsequently oxygen-delignified to a kappa number of about 12 with a viscosity of 1020 dm^3/kg , was treated with EDTA at 70°C for 60 minutes. The charge of EDTA was 2 kg per ton of dry pulp and the pH of the liquid was about 6. After the treatment, the mixture was diluted with pure water and the pulp was pressed to different dry matter contents so that washing efficiencies of 85%, 90% and 95% were obtained. Pulp containing 15%, 10% and 5% of filtrate from the original EDTA-stage were subsequently bleached under conditions which were otherwise identical with 35 kg

H₂O₂ per ton of pulp at 90°C for 270 minutes and at a pH of about 11.

Table 1

<u>Washing efficiency</u>	<u>H₂O₂ used kg/BDMT</u>	<u>Kappa number</u>	<u>Bright-ness % ISO</u>	<u>Viscosity dm³/kg</u>
85	34.5	5.1	74.7	847
90	34.3	5.0	75.0	828
95	31.0	4.6	77.7	869

As is evident from Table 1, the washing efficiency of 95% gives the best result for the process, with the lowest consumption of chemicals and the lowest kappa number, i.e. the most effective delignification and the greatest brightness together with the highest pulp viscosity, i.e. with the least effect on the cellulose.

The result indicates that the washing efficiency should be 90-95%. It should be pointed out, however, that pulps with lower initial content of heavy metals may give a good bleaching result even with lower washing efficiencies. Nevertheless, the washing efficiency should not fall below about 85%. In order to achieve this result, the washing equipment after the Q-stage should give at least this efficiency, preferably though 90-95%.

Additional comments concerning a bleaching plant according to Figure 1 are given below, as, in some measure, are directions regarding alternatives to the example shown.

Figure 1 shows a 2-stage washing apparatus after the Q-stage, a KAMYR® 2-stage diffuser. The washing efficiency with this apparatus is about 95%. In this diffuser, the filtrate from the subsequent peroxide stage is used as the washing liquid for stage 2. The additional displacement is about 2 tons of liquid per ton of pulp. If the pulp concentration in

the Q-stage is 10%, the amount of liquid employed is 9 tons per ton of dry pulp. With the additional displacement, the total discharge from the Q-stage becomes about 11 tons of liquid per ton of dry pulp. This quantity of filtrate is the only filtrate leaving the bleaching system. It contains released organic substances from the P- and Z-stages, spent bleaching chemicals and heavy metals released in the Q-stage. The filtrate can be concentrated by evaporation, for example by so-called mechanical vapour compression at reduced pressure. The filtrate can also be concentrated by so-called freeze-crystallisation, in which pure water crystals are formed and are separated off while released dry matter remains in the enriched filtrate, which can be conducted to the recovery system of the factory.

The recovery system can vary. For example, a portion of the filtrate can be used for dissolving the soda smelt from the recovery boiler. The remainder of the filtrate can be concentrated and mixed with the black liquor. If required, the whole of the filtrate can be subjected to a limited pre-evaporation or freeze-crystallisation to a liquid quantity which is adapted to the maximum quantity which can be fed to the soda dissolvers.

Alternatively, the whole of the filtrate can be pre-evaporated to the lowest possible quantity of liquid, which is then mixed with the black liquor, which goes to the usual evaporation system of the factory.

In order to limit energy consumption in the pre-evaporation stages or in the freeze-crystallisation system, the quantity of filtrate leaving the washing apparatus of the Q-stage can be decreased by reusing a portion of this filtrate as dilution liquid prior to the Q-stage. In this case, to achieve a balance in liquid management, the supply of fresh water to the

washing apparatus of the peroxide stage must be decreased to a corresponding degree and replaced with recirculated filtrate from the ozone stage. The degree of closure which is possible will depend on how many metal ions are introduced in the Q-stage together with the oxygen-delignified pulp.

As a result of the closure, an enrichment of both metal ions and released organic substances occurs in the filtrate of the Q-stage. Owing to this, the washing losses are increased over to the peroxide stage, which can impair the bleaching result. For pulps which do not have too high a content of heavy metals, and at low kappa numbers, the discharge from the Q-stage can be decreased to about 3 tons per ton of pulp by recirculation. In this way, a substantial decrease is obtained in necessary energy consumption in the pre-evaporation or freeze-crystallization systems. The supply of fresh water to the washing apparatus of the peroxide stage must be decreased to a corresponding degree and replaced with re-circulated filtrate from the Z-stage.

The peroxide stage is carried out at high temperature, 80-90°C, while the temperature in the subsequent ozone stage should not exceed about 50°C, in order to avoid too great a decrease in the viscosity, and hence the strength, of the bleached pulp. To avoid transfer of hot liquid from the peroxide stage to the ozone stage, the thermal efficiency in the washing apparatus after the peroxide stage should be high, over 85%, and preferably 90% or as high as 95%.

Additionally, it is important that the carryover to the ozone stage of dry material and residual chemicals released in the peroxide stage is as small as possible. Otherwise, ozone is consumed in the oxidation of material already released from the pulp instead of releasing further lignin from the pulp fibre. For this reason, too, the degree of washing

after the peroxide stage should be as high as possible and higher than 85% but preferably 90% and more preferred 95%.

A third justification for efficient washing after the peroxide stage is that unused peroxide, H_2O_2 , is effectively recirculated to the beginning of the peroxide stage by using filtrate from the washing stage after the peroxide stage as washing liquid for the washing apparatus after the Q-stage.

Figure 1 shows a KAMYR® 2-stage diffuser as washing apparatus after the peroxide stage. This apparatus gives a total washing degree of about 95% and thereby fulfills the above-specified requirements for washing efficiency. Besides temperature regulation, decreased carryover of released dry material and recirculation of residual chemicals, improved heat economy is also achieved by enclosing the peroxide stage between two washing devices of high washing efficiency.

By raising the thermal efficiency from 85% to about 95%, the quantity of steam required for the heat exchanger for filtrate from the washing apparatus after the peroxide stage for the washing apparatus after the Q-stage can be decreased by more than 30%.

When using alkaline filtrate from the peroxide stage as washing liquid for the washing apparatus after the Q-stage, there is a risk of reprecipitation of metal ions which have been chelated with EDTA. To achieve the best result, the pH in the Q-stage must be 5-6. The filtrate from the peroxide stage has a pH of 10-11.

The risk of reprecipitation can be substantially decreased by carrying out the wash after the Q-stage in two steps and by limiting the quantity of alkaline liquid which is transferred to the first washing stage to the dilution factor, i.e. about 2 tons. In order completely to eliminate any possible effect of this relatively low input of alkali, the

washing liquid from stage 2 to stage 1 can be neutralised by the addition of sulphuric acid (H_2SO_4).

Preferably, pure water at a temperature of 40-45°C is used as the washing liquid for the washing apparatus of the peroxide stage. If the thermal efficiency of the wash is sufficiently high, 90-95%, the temperature of the ozone stage will be 45-50°C. A higher temperature should be avoided in order to decrease the risk of impairing the quality of the pulp.

The pH of the pulp suspension in the ozone stage should be pH 2.0-3.0. This is achieved by adding sulphuric acid, H_2SO_4 , to the pulp prior to the stage. The filtrate which is drawn off from the wash after the ozone stage thus has a correspondingly low pH. This filtrate is suitable for adding to the last washing apparatus after the oxygen stage. This apparatus should preferably be a washing press or other apparatus which gives an outgoing pulp consistency in the region of 20-35%.

The filtrate of the ozone stage is used partly as washing liquid for the washing press and partly for diluting the pulp consistency entering the Q-stage from 20-35% to about 10%.

That part of the filtrate of the ozone stage which is used as washing liquid should be neutralised to about pH 6 in order to avoid lignin reprecipitation in the washing system after the oxygen stage.

As has been pointed out previously, the pH in the Q-stage should be pH 5-6. If required, additional sulphuric acid is added to adjust the pH. If, on dilution with the pulp from the last washing stage after oxygen delignification, the acid filtrate from the ozone stage gives a lower pH than about 5, it may become necessary to add alkali (NaOH) to adjust to a pH of 5-6.

If the bleaching is concluded after the ozone stage and is limited to the sequence QPZ, backwater

from a drying machine or possibly fresh water at a temperature of 40-60°C, preferably 45-55°C, is supplied to the washing apparatus after the ozone stage. This apparatus can have a somewhat lower washing efficiency than the washers after the Q- and P-stages. In Figure 1 a 1-stage diffuser has been included which gives a washing efficiency of 85-90%.

To stabilise the brightness of the pulp and destroy residual ozone after the ozone stage, sulphur dioxide can, if required, be supplied to the pulp suspension after the ozone-stage reactor but before the washing apparatus of this stage. If required, alkali (NaOH) is also added for neutralisation to pH 5-6.

If the highest brightness, 88-90 ISO, is required, an additional peroxide stage can be introduced after the ozone stage. The bleaching sequence then becomes QPZP. The last peroxide stage should have a temperature of 50-65°C. The charge of peroxide used must be low, 1-3 kg H_2O_2 per ton of pulp. The washing after the stage can be carried out, for example, by a 1-stage diffuser. The filtrate from this washing apparatus is used as the washing liquid for the washing apparatus after the ozone stage. The washing liquid used is backwater from the drying machine or pure washing water at a temperature of 45-55°C.

Bleaching conditions such as chemical charge, reaction temperature, dwell time, etc., will vary depending on the bleachability of the oxygen-bleached pulp. The example below demonstrates the difference between two different pulps, a pulp produced from Scandinavian softwood and a hardwood pulp produced from eucalyptus wood.

Table 2

	Softwood	Eucalyptus
Kappa number after oxygen stage	12	7.4
Viscosity dm ³ /kg	1020	998
<u>Q-stage</u>		
EDTA kg/ADMT	2.0	2.0
pH	6	5.4
<u>P1-stage</u>		
H ₂ O ₂ kg/ADMT	35	20
NaOH kg/ADMT	25	18
Temperature °C	90	80
pH	11.0	11.3
Viscosity dm ³ /kg	895	932
Brightness, ISO	78.1	81.8
<u>Z-stage</u>		
Ozone O ₃ kg/ADMT	4.7	3.9
pH	2.4	2.8
Viscosity dm ³ /kg	791	761
Brightness, ISO	86.5	89.4
<u>P2-stage</u>		
H ₂ O ₂ kg/ADMT	2	-
NaOH kg/ADMT	4	-
Temperature °C	70	-
pH	10	-
Viscosity dm ³ /kg	755	-
Brightness, ISO	90.2	-

As is evident from Table 2, for softwood pulp four bleaching stages with the sequence QPZP are required in order to achieve a brightness of 90 ISO, while with eucalyptus wood virtually the same brightness is achieved with only three bleaching stages, QPZ. In addition the consumption of bleaching agents is lower for this latter pulp type. This is due partly to the lower initial kappa number, but also to the fact that this type of pulp is easier to bleach even when starting from the same kappa number.

For softwood, the amount of COD, Na⁺ and dry matter (DM) in the combined filtrates from the different bleaching stages was

$$\text{COD} = 38.8 \text{ kg/ADMT}$$

$$\text{Na}^+ = 23.1 \text{ kg/ADMT}$$

$$\text{DM} = 99.0 \text{ kg/ADMT}$$

Using the described method of water management, and depending on the degree of closure and the quantity of filtrate going to evaporation and thence to chemical recovery, the following concentrations are obtained in the filtrate for 5 tons of filtrate per ton of pulp and 10 tons of filtrate per ton of pulp, respectively

Quantity of filtrate ton/ADMT	COD %	Na ⁺ %	DM %
5.0	0.77	0.46	1.90
10.0	0.39	0.23	0.98

It is evident that the concentration of dry matter in the filtrate is quite low, about 1% in the case of 10 tons of filtrate per ton of pulp and about 2% if the quantity of filtrate is decreased to 5 tons/ton of pulp. If the quantity of filtrate is decreased by evaporation or freeze-crystallisation to 0.5 tons per ton of pulp, the corresponding concentration then becomes about 16%, i.e. about the same concentration as in the black liquor which goes for evaporation. The increased load on the evaporation

plant which 0.5 tons of extra filtrate represents should in most cases not cause any problems with capacity. The proposed system should thus provide favourable conditions for solving the problem of restricting the effluent systems of the pulp factories and thereby radically improving the environmental situation.

It will be evident to the person skilled in the art that the invention is not limited to that which has been described above, but can be varied within the scope of the subsequent patent claims. Thus, it is, for example, possible for the dry matter in the drawn-off filtrate to be concentrated by some other method than that mentioned in Claims 3, 4 and 5, for example by osmosis, etc. In other respects as well it is evident that the person skilled in the art can employ various types of apparatus to achieve what is sought by the invention, for example other known washing devices can be used, for example a pressure diffuser, filter, etc., as alternatives to the washing press (before the Q-stage) shown. In addition, washing presses can be used instead of diffusers at certain points, for example after the Q-stage and/or the P-stage. Furthermore, it is possible to use something other than a P-stage as the fourth bleaching stage, for example a hydrosulphite-stage.

- 1) $\frac{(X-Y)}{X} \cdot 100$; where X is the quantity of undesirable substance before washing and Y is the quantity of the said substance remaining after washing, for a given amount of pulp.

PATENT CLAIMS

1. Process for bleaching pulp which has been digested and oxygen-delignified, using methods which preserve viscosity and strength, to kappa numbers lower than 16, preferably 12 and lower, more preferred lower than 10, without using chlorine-containing chemicals and employing a bleaching sequence containing at least 3 bleaching stages, whose first three stages are QPZ, characterised in that

the total filtrate quantity leaving the bleaching plant is limited to at most 10 tons of liquid per ton of 90% pulp, preferably to at most 7 tons of liquid per ton of 90% pulp, and more preferred to at most 5 tons of liquid per ton of 90% pulp, and even more preferred to at most 3 tons of liquid per ton of 90% pulp,

the filtrates from the different bleaching stages are managed in such a way that the major part of all the liquid from the bleaching plant is drawn off from the washing apparatus after the Q-stage,

the washing devices after both the Q- and P-stages have a washing efficiency of at least 85%, preferably at least 90, and more preferred at least 95%,

the filtrate from the washing apparatus after the P-stage is recirculated and used as washing liquid for the washing apparatus after the Q-stage,

washing water at a temperature of 40-55°C, preferably 45-50°C, is supplied to the washing apparatus after the P-stage,

the filtrate from the Z-stage is used for washing in the last washing apparatus after the oxygen stage before the bleaching sequence QPZ.

2. Process according to Claim 1, characterised in that the filtrate drawn off from the bleaching plant is

supplied to the chemical recovery system of the factory for combustion of organic material and recovery of inorganic chemicals.

3. Process according to Claim 2, characterised in that, before transfer to the chemical recovery system, the filtrate is wholly or partly pre-evaporated in a separate evaporation plant, for example according to the vapour compression principle, and preferably that evaporated water is used within the factory.

4. Process according to Claim 2, characterised in that, before transfer to the chemical recovery of the factory, the filtrate is subjected to so-called freeze-crystallisation and preferably that pure water which has been separated off is used for the needs of the factory.

5. Process according to Claim 2, characterised in that the dry matter in the filtrate which has been drawn off is concentrated by ultrafiltration.

6. Process according to Patent Claim 1, characterised in that the filtrate drawn off from the Q-stage is used in part for diluting the pulp entering this same stage.

7. Process according to Patent Claim 6, characterised in that the quantity of fresh water for the washing stage after the P-stage is decreased to a corresponding degree and is replaced with filtrate from the washing apparatus of the Z-stage.

8. Process according to Claim 1, characterised in that KAMYR's 2-stage diffusers are used as the washing apparatus after the Q- and P-stages.

9. Process according to Claim 1, characterised in that KAMYR's 1-stage diffusers are used as washing devices after the Z-stage and a P-stage which may optionally follow it.

10. Process according to Claim 1, characterised in that backwater from a drying machine or pure water is used as the washing liquid after the Z-stage or a P-

stage which may optionally follow it.

11. Process according to Claim 1, characterised in that the filtrate from the last P-stage is used as the washing liquid for the Z-stage in the sequence QPZP.

12. Process according to Claim 1, characterised in that sulphur dioxide (SO_2) and, if necessary, alkali (NaOH) are supplied to the pulp after the reactor of the ozone stage and before the washing stage.

13. Process according to Claim 8, characterised in that acid, preferably sulphuric acid, is added to the liquid which is conducted from the second stage of the 2-stage diffuser of the Q-stage to the first stage of the same apparatus and that the pH of the liquid is adjusted to pH 5-6.

14. Process according to Claim 1, characterised in that a washing press is used as the preferred washing apparatus after the oxygen stage and that, in this connection, the filtrate from the Z-stage is also used for diluting the pulp for the Q-stage.

15. Process according to Claim 1, characterised in that the bleaching plant contains an additional bleaching stage, a fourth stage, preferably in the form of a P-stage.

6. Process according to Claim 15, characterised in that the additional bleaching stage consists of a hydrosulphite stage.

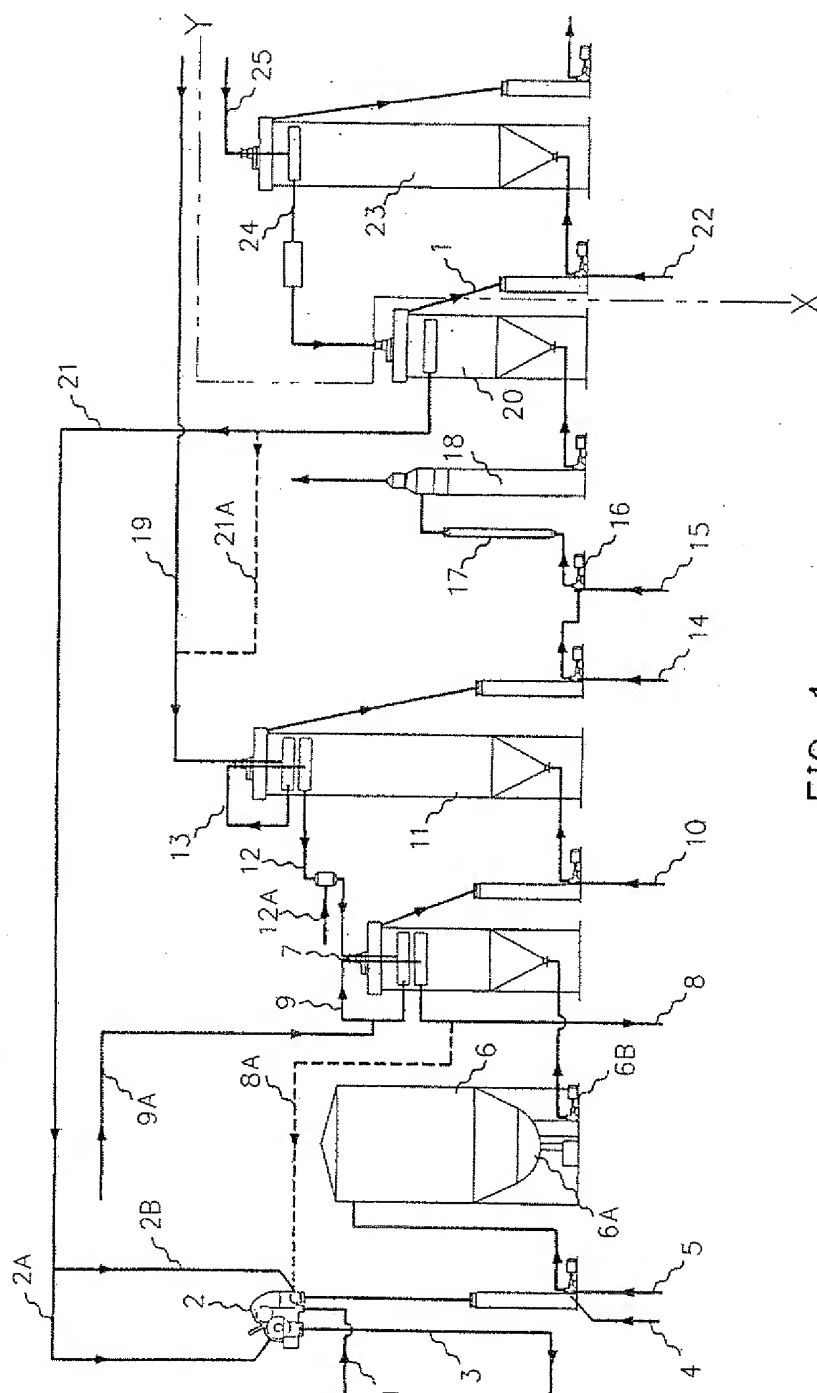


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SE 93/00312

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: D21C 9/10, D21C 9/16, D21C 9/153

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	EP, A1, 0512590 (EKA NOBEL AB), 11 November 1992 (11.11.92), claims 1-2 --	, 1-16
A	EP, A2, 0402335 (EKA NOBEL AKTIEBOLAG), 12 December 1990 (12.12.90) --	1-16
A	WO, A1, 9118145 (UNION CAMP CORPORATION), 28 November 1991 (28.11.91), figure 4 -- -----	1-16

☐ Further documents are listed in the continuation of Box C.
 ☒ See patent family annex.

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

23 August 1993

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INTERNATIONAL SEARCH REPORT
Information on patent family members

30/07/93

International application No.
PCT/SE 93/00312

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A1- 0512590	11/11/92	AU-A- 1514892 JP-A- 5148785 SE-B- 468355 SE-A- 9101300	11/03/93 15/06/93 21/12/92 31/10/92
EP-A2- 0402335	12/12/90	AU-B- 613272 AU-A- 5621790 CA-A- 2017807 JP-A- 3027191 SE-B, C- 467006 SE-A- 8902058	25/07/91 07/02/91 06/12/90 05/02/91 11/05/92 07/12/90
WO-A1- 9118145	28/11/91	EP-A- 0483163	06/05/92